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NATIONAL WATER QUALITY NETWORK. REPORT ON ANALYTICAL REFERENCE SAMPLE TYPE I, BD-4

Robert A. Taft Sanitary Engineering Center
Cincinnati, Ohio

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NATIONAL WATER QUALITY NETWORK

report on analytical reference sample

TYPE I, BD-4

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HEALTH, EDUCATION, AND WELFARE
Public Health Service
ROBERT A. TAFT
SANITARY ENGINEERING CENTER
Cincinnati, Ohio

Participants in Study of Type I - HD-4
(Distributed June 1, 1959)

Bismarck Water Department
Bismarck, North Dakota

North Dakota State Dept. of Health
Public Health Laboratory
Bismarck, North Dakota

Boulder City Water Plant
Boulder City, Nevada

Erie County Laboratory
Buffalo, New York

Cairo Water Company
Cairo, Illinois

Crown Zellerbach Corp.
Central Research Department
Camas, Washington

Missouri Utilities Company
Cape Girardeau, Missouri

City Water Company
Chattanooga, Tennessee

Tennessee Valley Authority
Stream Pollution Control Laboratory
Chattanooga, Tennessee

City Water Department
Cincinnati, Ohio

Municipal Laboratory
Denison, Texas

Board of Water Commissioners
Water Works Park Filtration Plant
Detroit, Michigan

Dubuque Water Department
Dubuque, Iowa

East Liverpool Water Department
East Liverpool, Ohio

East St. Louis Water Company
East St. Louis, Illinois

Water Treatment Plant
El Paso, Texas

Gary-Hobart Water Corp.
Gary, Indiana

Hagerstown Water Department
Hagerstown, Maryland

Huntington Water Corporation
Huntington, West Virginia

Board of Public Utilities
Kansas City, Kansas

City Water Department
Laredo, Texas

Massachusetts State Dept. of Health
Lawrence Experiment Station
Lawrence, Massachusetts

Arkansas Water Pollution Control Comm.
Little Rock, Arkansas

City of Memphis
Light, Gas and Water Division
Memphis, Tennessee

Chemical-Toxicological Laboratory
Louisiana State Health Department
New Orleans, Louisiana

North Augusta Water Department
North Augusta, South Carolina

Metropolitan Utilities District
Omaha, Nebraska

Mississippi State Board of Health
Chemical Laboratory
Jackson, Mississippi

//

Participants (Cont'd)

City Water Department
Pasco, Washington

Torresdale Laboratory
Philadelphia Water Department
Philadelphia, Pennsylvania

Oregon State Sanitary Authority
Portland, Oregon

International Business Machines Corp.
Poughkeepsie, New York

School of Engineering
Washington State College
Pullman, Washington

City of St. Louis Water Dept.
St. Louis, Missouri

Minneapolis-St. Paul Sanitary District
St. Paul, Minnesota

Montana-Dakota Power Company
Sidney, Montana

Union Bag-Camp Paper Corp.
Savannah, Georgia

St. Joseph Water Company
St. Joseph, Missouri

St. Louis County Water Co.
University City, Missouri

Corps of Engineers
Dalecarlia Filtration Plant
Washington, D. C.

Weiser Water Department
Weiser, Idaho

Aluminum Company of America
Wenatchee, Washington

City Water Department
Williston, North Dakota

Yankton Water Department
Yankton, South Dakota

Arizona Water Company
Yuma, Arizona

INTRODUCTION

Much of the physical and chemical data accumulated by the PHS National Water Quality Network are the result of the cooperative efforts of many laboratories located at or near the sampling sites. Because these analyses originate from so many different sources, it is essential that they be comparable as to accuracy. The reference sample technique is a mechanism by which this objective can be achieved. Reference samples are being submitted periodically to each of the cooperating laboratories to insure continued accuracy of the data submitted.

REPORT ON THE ANALYTICAL REFERENCE SAMPLES TYPE I, BD-4

Sample Type I, BD-4 is the fourth in a series of standard samples representative of the mineral analyses being reported to the Water Quality Program. Fifty laboratories received this sample and 45 have reported in time to have their results included in this report. Most laboratories have little or no difficulty in performing these examinations, as confirmed by the general excellence of the reported results.

The individual analyses are presented in Table II and the bar graphs. The dotted lines on the graphs represent limits of accuracy for this sample which are acceptable to the Program. The selection of these limits was influenced by the accuracy with which each test can be performed, as determined by "Standard Methods" as well as the needs of our program. In most cases, those laboratories falling outside the acceptable range were notified immediately and requested to review the procedures used in order to determine the reasons for the discrepancies.

It is strongly urged that all cooperating laboratories furnish comments on the analytical methods used. A complete log of pertinent details, difficulties, modifications, sources of error, and other factors affecting the precision and accuracy of the analytical procedures would be extremely valuable in the development of simpler and more accurate analytical procedures. This report may also be useful as a means of self-evaluation by each of the participating agencies. Assistance on laboratory procedures is available to the cooperating laboratories from the Public Health Service, through its Regional Offices or the Sanitary Engineering Center.

DISCUSSION OF RESULTS

Statistical comparisons in this report were developed from the deviations from known quantities added to the sample. The range of deviations considered acceptable to the program were based on the precision and accuracy values as presented in "Standard Methods" for the various tests involved. Table I, below, is a summary of the expected accuracy for the various tests from "Standard Methods" and the ranges acceptable for the Water Quality Network for this reference sample.

Laboratories reporting values outside the range of acceptability should investigate their procedures for sources of error. Have standard solutions been checked recently? Are the reagents too old? Are sample sizes adequate for maximum accuracy? How carefully are weighings being made? Are standard curves being checked frequently? Although most of these tests are simple and "routine", a thorough review of the details in each procedure may disclose errors which have become habitual and escape unnoticed during routine operations.

TABLE I

Acceptable Limits of Accuracy

	Standard Methods	Water Quality Program
Chloride 100 ml sample	± 1.0 mg/l	± 2.0 mg/l
Sulfate Turbidimetric	± 10%	± 10%
Alkalinity 50 ml sample	± 2.0 mg/l	± 4.0 mg/l
T.D.S. 200 ml sample	3 mg/l	± 21 mg/l
Hardness 50 ml sample	± 2 mg/l	± 4.0 mg/l
pH	± 0.1 unit	± 0.2 unit
Turbidity	-	± 32 units

The Tenth Edition of "Standard Methods" gives the expected precision and accuracy for each test, within the range of concentration normally encountered in water analysis. These "standards of accuracy" should be attainable by most laboratories performing these routine examinations. The additional errors, allowable for the Network Program, are intended only as a guide to the cooperating laboratories and are not to be considered as the ultimate goal in the achievement of laboratory accuracy. The limits allowed in this report are narrower than those allowed in previous reference samples, and they will continue to be revised upward as more and more laboratories continue to improve their performance through experience gained in the Program.

CHLORIDE - 43 mg/l

Although several methods are available for this determination, 29 of 38 laboratories used the Mohr procedure. The most frequent criticism of this method is the obscurity of the real end point due to the presence of the Silver Chloride precipitate. A frequent, but minor error is failure to correct for the indicator blank. The use of a yellow light aids in detecting the endpoint. The chief precaution to be observed in this determination, as in any volumetric procedure, is standardization of reagents. Seventeen of the 38 laboratories reporting this analysis fell within + 2 mg/l of the known value. Eight additional laboratories fell within + 4 mg/l but only ten were within + 1 mg/l of the known value. It is of interest to note that of the 5 laboratories using the Mercuric Nitrate method, 4 were within the allowable limits and the other lab was only 1 mg/l beyond. From the symmetrical distribution of results, it is evident that many laboratories can easily perform the chloride determination within the limits of precision, but some of the other analysts might do well to investigate a different procedure, particularly the mercuric nitrate titration.

SULFATE - 40 mg/l

Seventeen of the 32 laboratories reporting this analysis fell within the allowable limits. Nine additional laboratories fell within double the allowable limits. Of the laboratories outside the acceptable range, one reported using the Tetrahydroxyquinone (THQ) procedure; one reported using the Benzidine Hydrochloride procedure; two reported using the gravimetric procedure; eight reported using the turbidimetric procedure; and the remainder did not specify the method used.

At higher sulfate concentrations, the gravimetric procedure is considered to be the more accurate, but at the concentration present in this sample the turbidimetric procedure should be equally satisfactory. Insufficient removal of turbidity from the sample before performing the sulfate analysis may account for some of the high results. The usual precautions of washing and drying precipitates also had to be observed to obtain good results on the gravimetric procedure. The turbidimetric procedure has the advantages of being less time consuming and more simple to perform.

TOTAL DISSOLVED SOLIDS - 424 mg/l

In the performance of the Total Dissolved Solids determination, no difficulties should normally be encountered. A measured volume of turbidity-free sample is placed in a dish, evaporated to dryness and weighed. Two precautions must be observed: (1) the turbidity must be completely removed, and (2) the sample must be taken to dryness at 103-105°C. Incomplete drying allows excessive amounts of water to be included in the final weighing which, along with turbidity particles, will cause high results. A third precaution, also related to drying, must be exercised. If the drying temperature is too high, certain materials, such as carbonates, bicarbonates, or chlorides may be partially volatilized and the result will be too low. For these reasons the precautions, while simple, must be strictly observed. The size of the sample taken for this test will influence its precision considerably. To achieve a satisfactory result the sample size should be large enough to produce a residue weighing not less than 25 mg in order that the precision of the weighing will fall within the acceptable range.

Of the 33 laboratories reporting this determination, 21 fell within the $\pm$ 21 mg/l range and 5 more were within double the acceptable range.

By referring to the bar graph for this analysis, it can be seen that the results farthest beyond the acceptable range are all on the high side which indicates the possibility of incomplete removal of turbidity particles. In fact, four of the results are excellent figures for total solids, which would include all of the turbidity. A very retentive filter, preferably a millipore, is required for complete removal of turbidity.

ALKALINITY - 47 mg/l (as $CaCO_3$)

This procedure allows a choice of indicators or electrometric measurement for the detection of the endpoint. Of the 43 laboratories reporting this analysis, 14 used methyl orange indicator; six used methyl purple; 11 used an electrometric endpoint; and one used Cooper's mixed indicator. The other 10 laboratories did not report the method used. Thirty-four of the reported results were within the allowable limits with 4 perfect results. Of the eight laboratories outside the acceptable range, three reported using methyl orange; two used methyl purple; one used the electrometric endpoint; and the others did not indicate the method of analysis. It is of interest that of the 11 laboratories using an electrometric endpoint, four reported using an endpoint of pH 4.6 and obtained results that deviated from the known value by -1, +1, +2, and -4 mg/l. One analyst used an endpoint at pH 4.0 and obtained a result that was 13 mg/l too high, while another analyst used an endpoint of pH 5.1 and obtained a result that was 3 mg/l low. The analysis using an endpoint of pH 4.0 was the only one of the electrometric titrations to fall beyond the acceptable range.

HARDNESS - 102 mg/l (as $CaCO_3$)

All laboratories that specified the procedure, employed some modification of the EDTA titration. Twenty-seven of the 42 laboratories fell within the acceptable limits with four perfect results. Six additional laboratories were within double the acceptable range. The majority of results outside the acceptable range were on the low side which may be due to incorrect pH adjustment of the sample before titration. The sample had a high buffer capacity and required more than the usual amount of buffer to raise the pH to the proper level. Other possible sources of error are improperly standardized reagent, miscalculation, or faulty indicator. It is suggested that the indicator, Eriochrome Black T, be used in dry form, mixed with sodium chloride.

HYDROGEN ION CONCENTRATION (pH) 6.9

The sample was made from a Clark and Lubs buffer and the pH was verified at the SEC by averaging the results from three carefully standardized pH meters. Of the 43 laboratories reporting this analysis, 39 fell within the acceptable limits with 11 perfect results. Only four laboratories fell outside the $\pm$ 0.2 range. Twenty-nine of the 31 laboratories that used a pH meter fell within the allowable limits; eight of the nine that used a colorimetric method were acceptable; and two of the three that did not specify the method were within the acceptable range. "Standard Methods" indicates that a precision of 0.1 pH unit is readily attainable with the glass electrode.

TURBIDITY - 325 Jackson Units

The turbidity value assigned to this sample was obtained by a series of readings on the Jackson Candle Turbidimeter following a period of aging after the sample was prepared.

Of the 40 laboratories reporting this analysis, 22 fell within the allowable limits. Of these, 19 used the Jackson Candle apparatus; one used the Hellige turbidimeter; one used a photelometer; and the other did not specify the method used. The larger deviations were all on the low side, which suggests the possibility that insufficient shaking of the sample might be the cause of the error, since the particles settled rapidly in this sample. Eight laboratories indicated that they used a Hellige instrument but did not indicate whether the value reported had been converted to Jackson units. When results are reported in terms of Hellige values, they are not comparable to the units selected for National Water Quality Network tabulations and they are therefore of little value to the network. Calibration of the Hellige instrument in terms of Jackson units is necessary. Those laboratories using instruments not so calibrated, are urged to ask for turbidity standards for this calibration from SEC.

TABLE II - SUMMARY OF RESULTS

ANALYTICAL REFERENCE SAMPLE TYPE I, RD-4

Analyses Performed	Chloride	Sulfate	T.D.S.	Alkalinity	Hardness	pH	Turbidity
Amount Added	43 mg/l	40 mg/l	424 mg/l	47 mg/l	102 mg/l	6.9	325
Lab #	Average Amount Reported by Each Lab						
SEC	41	40	424	48	100	6.9	325
1	35	—	-	48	97	6.9	327
2	50	40	428	47	100	6.9	126*
3	40	—	-	46	95	6.9	363
4	46	45	386	43	86	7.0	290
5	35	45	354	-	-	-	-
6	45	33	1000*	44	100	6.7	308
7	38	28	-	43	100	6.9	87*
8	37	—	-	51	97	6.8	307
9	48	48	400	47	80	6.8	320
10	27*	—	-	53	92	7.1	320
11	47	40	400	55	99	6.8	247
12	50	43	419	50	102	6.8	300
13	49	413*	1065*	48	102	6.8	273
14	41	43	430	54	101	6.8	335
15	42	43	414	51	101	6.9	315
16	44	38	410	46	104	6.9	333
17	47	32	375	51	97	6.9	365
18	—	—	-	49	100	6.6	195*
19	—	—	-	50	100	7.1	277
20	39	41	423	53	104	6.9	270
21	42	31	412	48	103	7.1	357
22	—	—	-	49	101	6.8	342
23	42	37	403	50	104	7.0	293
24	48	44	434	46	102	6.9	312
25	—	—	1078*	49	102	6.9	-
26	44	49	434	51	107	7.0	315
27	43	49	405	47	99	6.8	303
28	43	—	397	48	105	7.0	271
29	43	39	418	48	100	6.8	300
30	41	—	-	51	90	6.7	123*
31	45	38	412	28	86	6.4	291
32[a]	40	31 40	415	60	101	6.9	303
33	46	37	442	46	105	6.7	122*
34	41	56	430	44	112	6.7	318
35	—	46	399	—	-	-	-
36	—	—	1034*	47	84	7.0	287
37	85*	—	-	44	103	6.4	-

TABLE II - SUMMARY OF RESULTS (Cont'd)

ANALYTICAL REFERENCE SAMPLE TYPE I, BD-4

Analyses Performed	Chloride	Sulfate	T.D.S.	Alkalinity	Hardness	pH	Turbidity
Amount Added	43 mg/l	40 mg/l	424 mg/l	47 mg/l	102 mg/l	6.9	325
Lab #	Average Amount Reported by Each Lab						
38	47	57	406	5[a]	106	6.8	302
39	—	—	-	51	107	6.7	310
41	41	37	435	44	103	6.8	313
42	41	40	407	48	104	7.0	297
43	43	39	424	48	99	6.6	270
44	4.0*	281*	836*	60	90	7.0	90*
45	36	38	413	55	90	7.0	367
46	43	-	-	54	98	6.8	-

[a] - Reported sulfate by two different methods.

TABLE III

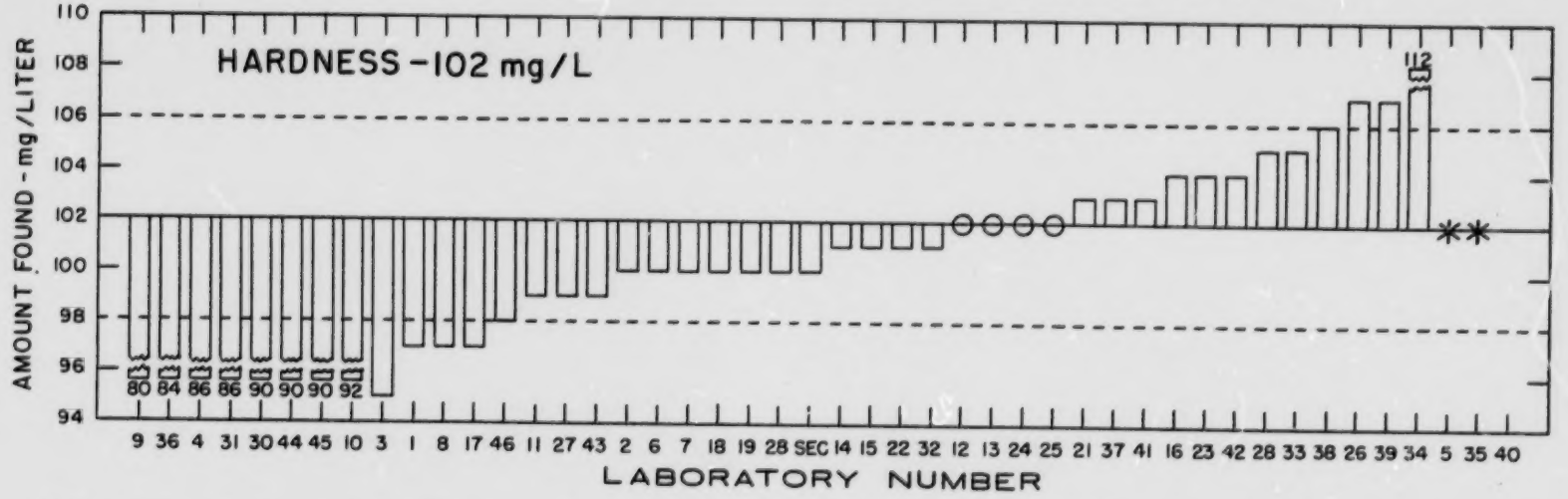
STATISTICAL SUMMARY OF RESULTS

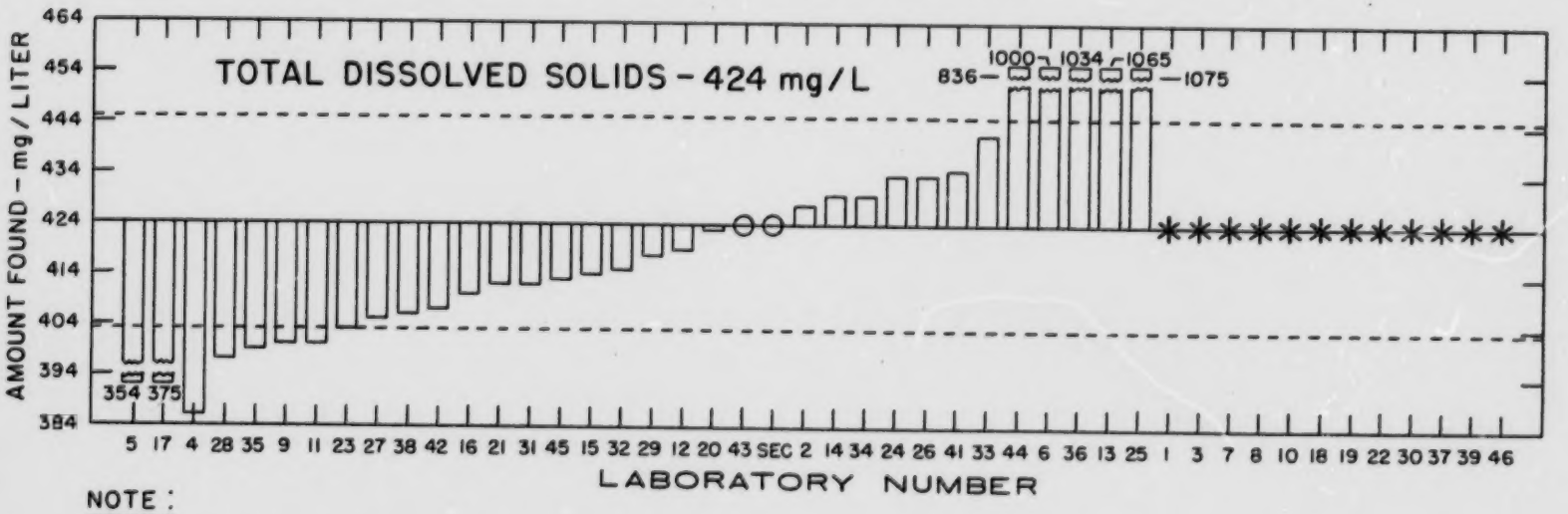
	Chloride	Sulfate	T.D.S.	Alkalinity	Hardness	pH	Turbidity
Amount added	43 mg/l	40 mg/l	424 mg/l	47 mg/l	102 mg/l	6.9	325
Number of Observations	35*	30*	28*	43	43	43	34*
Mean	42.9 mg/l*	40.9 mg/l*	411.6 mg/l*	48.7 mg/l	99.0 mg/l	6.84	308.9*
Median	43 mg/l	40 mg/l*	412 mg/l	48 mg/l	100 mg/l	6.9	308*
Standard deviation from mean	4.0*	6.7	19.0	5.2	7.9	0.28	28.4*
95% Confidence Limit	*43±8.1	41±13.7	412±38.9	49±10.5	99±16.0	6.8±0.57	*309±57.8
50% Confidence Limit	*43±2.7	41±4.6	412±13.0	49±3.6	99±5.4	6.8±0.19	*309±19.4
Range	*35-50	28-57	354-442	28-60	80-112	6.4-7.1	*247-367

*Results were not included in the computation due to obvious arithmetical or manipulative errors.

NATIONAL WATER QUALITY NETWORK

ANALYTICAL REFERENCE SERVICE SAMPLE TYPE I, BD-4





NOTE:

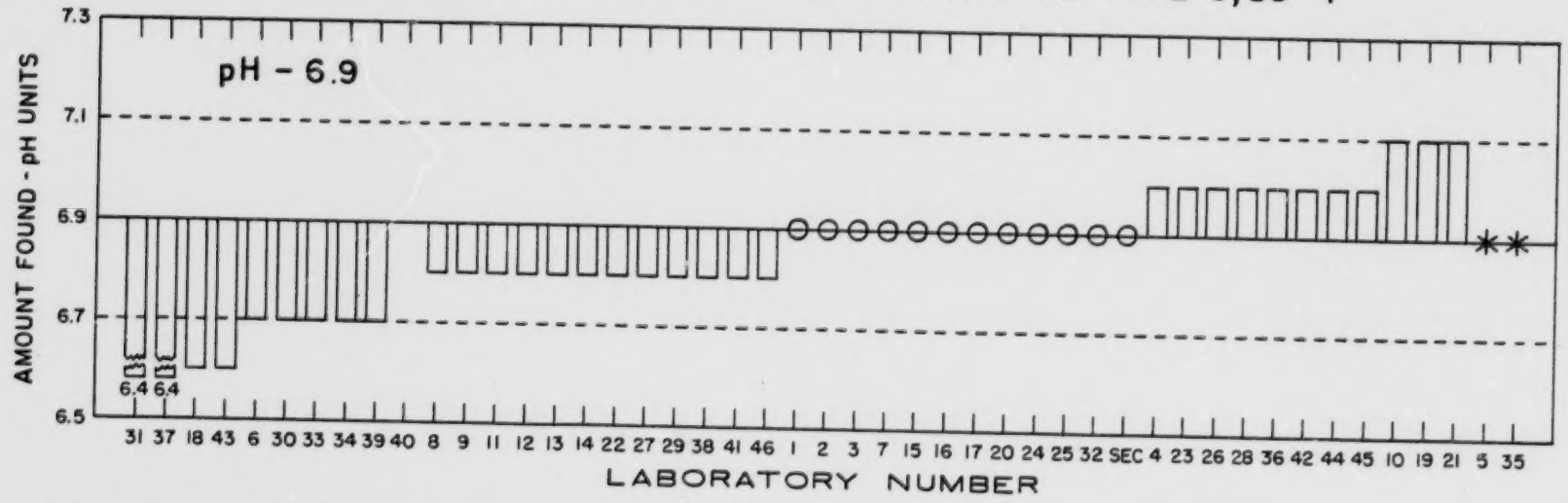
O — PERFECT RESULTS

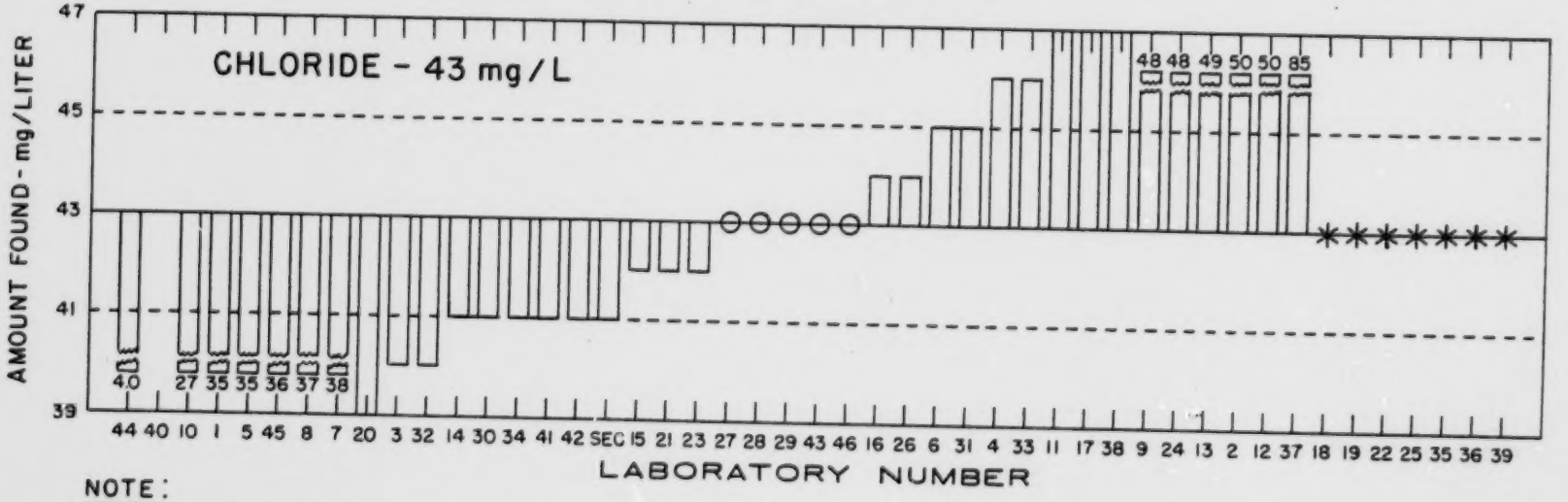
✱ — NO ANALYSIS PERFORMED

----- ACCEPTABLE LIMITS OF ACCURACY

NATIONAL WATER QUALITY NETWORK

ANALYTICAL REFERENCE SERVICE SAMPLE TYPE I, BD-4





NOTE:

O — PERFECT RESULTS

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----- ACCEPTABLE LIMITS OF ACCURACY

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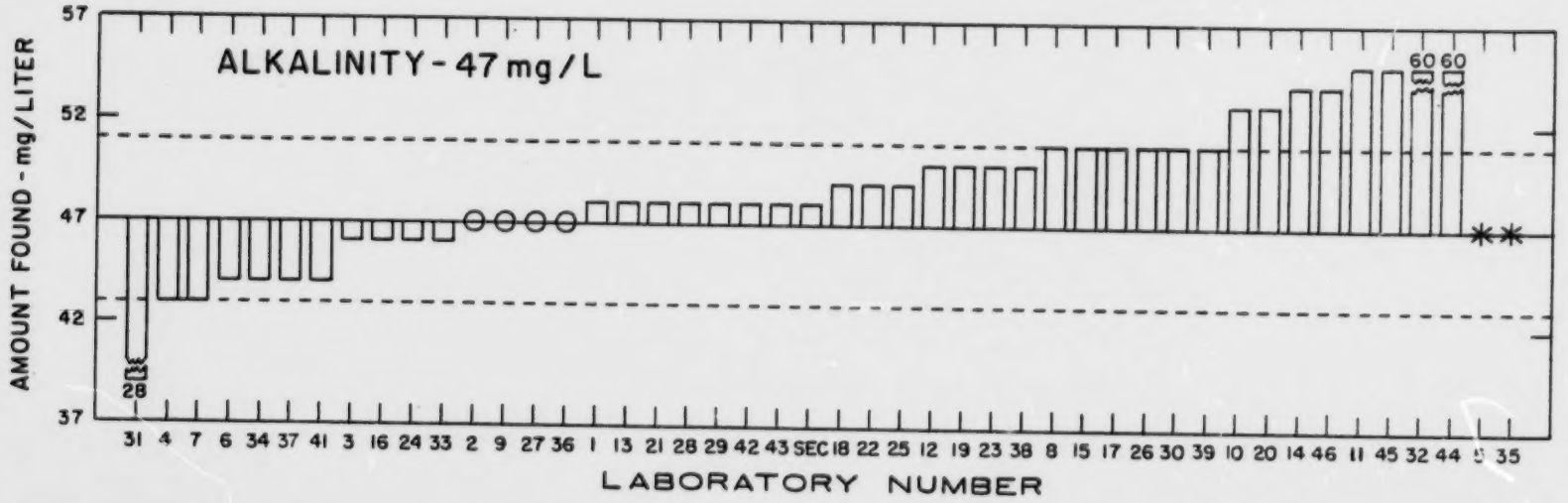
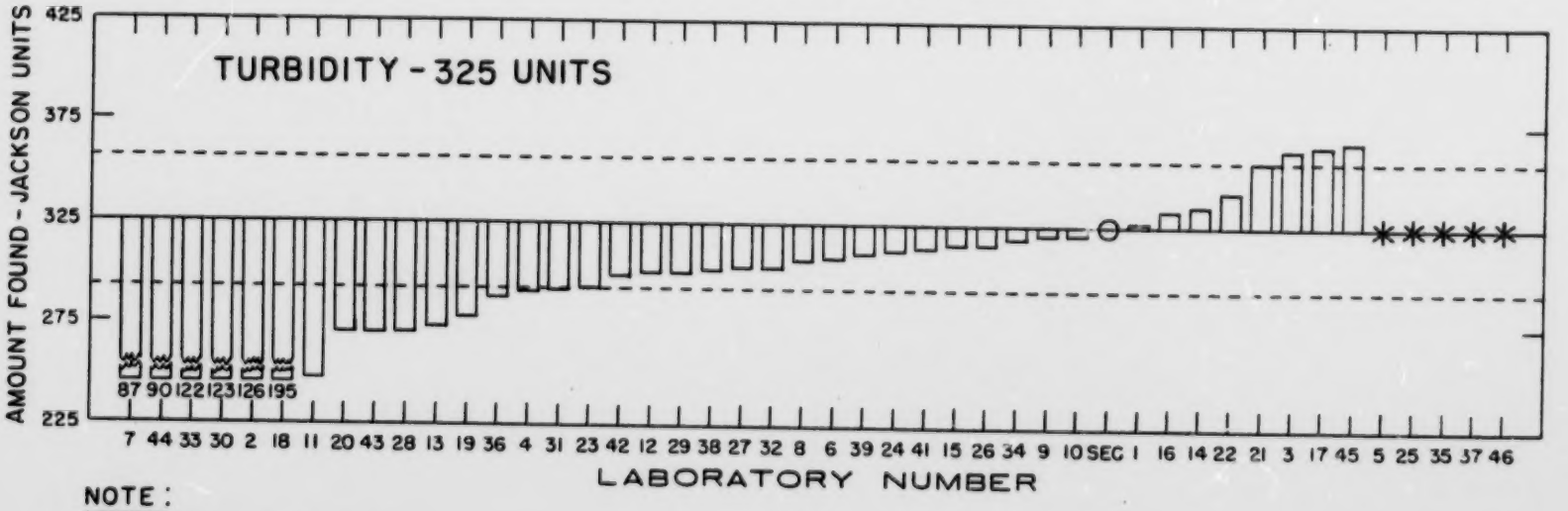
ANALYTICAL REFERENCE SERVICE SAMPLE TYPE I, BD-4





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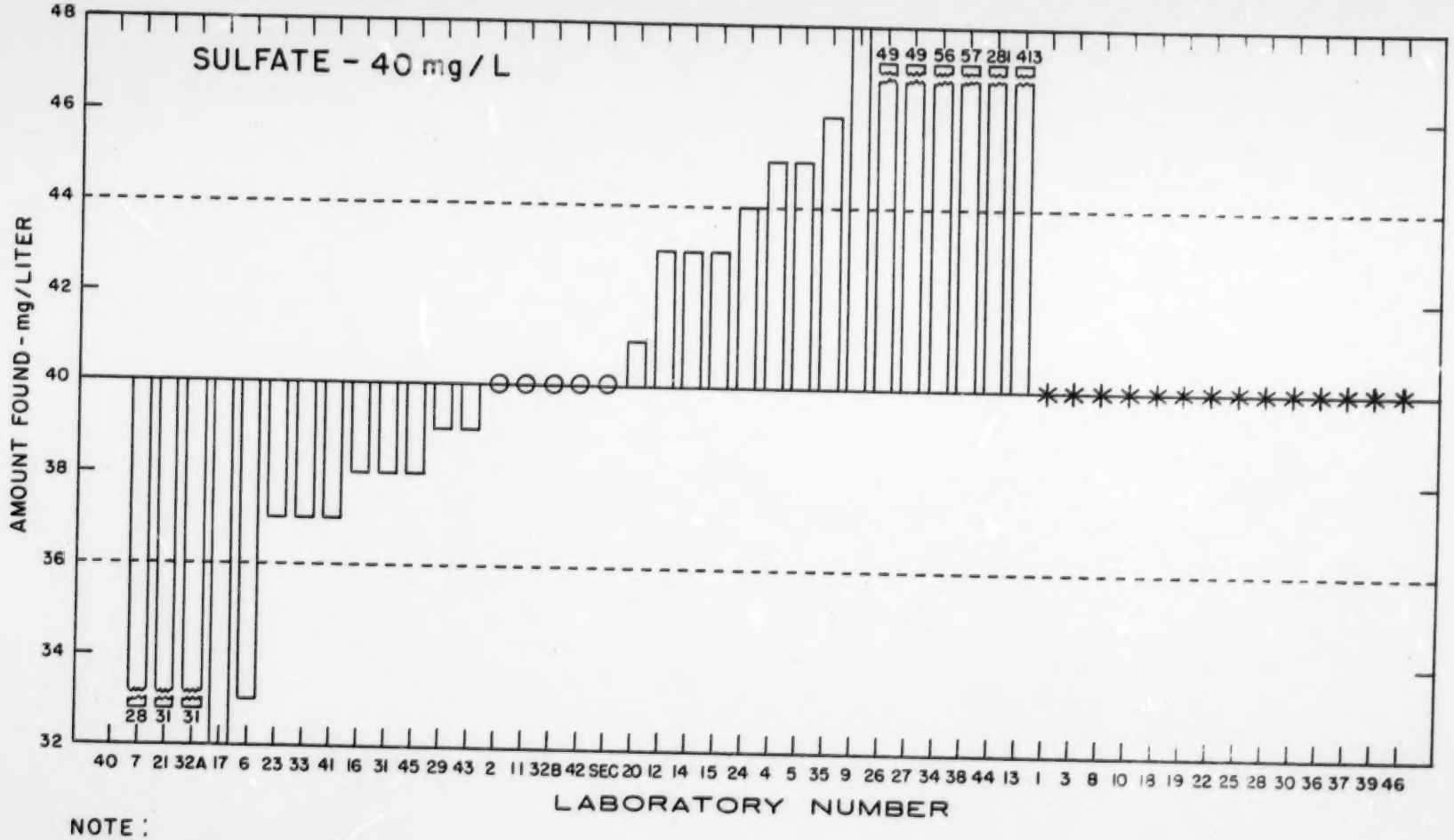

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----- ACCEPTABLE LIMITS OF ACCURACY

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